

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | |
|--|-----------|---|
| (51) International Patent Classification : Not classified | A1 | (11) International Publication Number: WO 97/40659 (43) International Publication Date: 6 November 1997 (06.11.97) |
| (21) International Application Number: PCT/SE97/00667 (22) International Filing Date: 21 April 1997 (21.04.97) (30) Priority Data: 9601594-6 26 April 1996 (26.04.96) SE (71) Applicant (for all designated States except US): ABB ATOM AB [SE/SE]; S-721 63 Västerås (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): DAHLBÄCK, Mats [SE/SE]; Mangelgatan 13, S-724 76 Västerås (SE). (74) Agent: LUNDBLAD VANNESJÖ, Katarina; Asca Brown Boveri AB, Patent, S-721 78 Västerås (SE). | | (81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: FUEL BOXES AND A METHOD FOR MANUFACTURING FUEL BOXES (57) Abstract A fuel box for a nuclear fuel bundle for a boiling water reactor is manufactured by zirconium alloy plates. The plates have a composition such that the material after beta quenching and heat treatment will have a ductile, so-called basketweave structure. | | |

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

FUEL BOXES AND A METHOD FOR MANUFACTURING FUEL BOXES

TECHNICAL FIELD

5 The present invention relates to the field of fuel boxes of a zirconium alloy for use in nuclear fuel assemblies intended for boiling water reactors, and to a method for manufacturing such boxes.

10 BACKGROUND ART

Nuclear fuel bundles for boiling water reactors are usually surrounded by a fuel box. The main functions of the fuel box are to provide mechanical stability to the bundle and to
15 conduct the cooling water such that adequate cooling of the fuel bundle in all its parts is obtained.

The fuel box has a square cross section and surrounds the bundle in all of its length. At the bottom of the fuel box a
20 transition piece is attached, and at the bottom thereof there is a guide intended to be arranged in the assembly supporting plate of the reactor. The box may also be provided with an inner, usually cruciform structure which axially divides the fuel bundle into four sub-bundles.

25 The accuracy of shape of the fuel box is of the utmost importance for its function. It is also important for the box to have good corrosion resistance during reactor operation. The box has large surfaces in contact with the reactor coolant.
30 Flaking corrosion products should not form on the box surfaces since these products may spread radioactivity to various systems in the reactor. There should also be a good margin with respect to weakening of the box wall caused by the metal being transformed into oxide.

35 During manufacturing of a fuel box, the starting material are thin rectangular plates of a zirconium alloy. Zirconium alloys

widely used in nuclear reactors are Zircaloy-2 and Zircaloy-4. Zircaloy-2 contains 1.2 to 1.7% tin, 0.07 to 0.20% iron, 0.05 to 0.15% chromium, 0.03 to 0.08% nickel, 0.09 to 0.16% O and Zircaloy-4 contains largely the same alloying elements but
5 lacks nickel and contains somewhat more iron, 0.018 to 0.24%. Also other zirconium alloys for reactor purposes such as, for example, a zirconium-base alloy containing about 1% tin, about 1% niobium and about 0.2% iron, or a zirconium alloy containing about 1% niobium, 1% tin, 0.5% iron and 0.2%
10 chromium may be used as starting material. The alloys also comprises incidental impurities, normally in the range of 500 to 1500 ppm.

The box is manufactured by bending two plates into U-shape.
15 The bending is carried out with a conventional method and may be preceded by a heat treatment of the plate to increase its ductility. Two U-shaped plates are turned so as to face each other and are welded together along the folded-up parts of the plates, so as to obtain a box with a square cross section. The
20 shaping of the box into the finished dimension is made by heat-treating the box on a device in a conventional manner.

To improve the corrosion properties of the material, it is known, according to GB 1 537 930 , to heat the material to a
25 temperature exceeding 900°C so that a phase transformation occurs in the material from hexagonal alpha phase to cubic beta phase, and thereafter to cool the material rapidly, so-called beta quenching. Phase transformation occurs at about 870°C, and above about 930°C the material is completely
30 transformed into beta phase. The temperature may vary somewhat depending on what alloying elements the zirconium contains, but all zirconium alloys for reactor purposes are low alloy elements so the variation in phase transformation temperature is relatively small.

35

From GB 1 537 930 it is clear that the plate is to be heated to a temperature of at least 900°C by allowing the temperature

rise from 500°C to the desired heat-treatment temperature and the heat treatment to take at most 60 seconds, whereafter the plate is to be cooled at least 200°C in at most 60 seconds. During cooling of the plate, the material forms an acicular structure, so called Widmanstätten structure.

US 4 238 251 describes heat treatment of nuclear fuel components for improving the corrosion resistance in boiling water reactors.

10

A fuel box in finished or almost finished form is heat-treated at a temperature so that an incipient phase transformation from alpha to beta takes place, whereupon the box is rapidly cooled to about 700°C. This heat treatment, so-called beta quenching, brings about a segregation of intermetallic particles in a two-dimensional pattern. The heat treatment is primarily to take place at a temperature higher than 965°C and should not occur at a temperature exceeding 1100°C since this is too energy-demanding without providing structural advantages compared with heat treatments at lower temperatures. The box should be maintained at the heat-treatment temperature for about 3 to 30 seconds and then be quenched to a temperature lower than 700°C at a rate of about 200°C per second.

25 US 5 361 282 also describes a heat treatment of zirconium plates for fuel boxes to achieve good corrosion resistance in a boiling-water reactor environment. The heat treatment means that the material is heated to 980°C to 1120°C and is kept at the heat-treatment temperature for 0.25 seconds to 30 minutes, whereafter the material is cooled down to a temperature lower than 815°C at a cooling rate of 6-240°C per second. The beta quenching heat treatment leads to a random distribution of the crystals in the hexagonal alpha structure. A random distribution of crystals will decrease the tendency of the fuel box to bow in reactor service.

35

A problem with the heat treatments which are conventionally used for improving the corrosion resistance of the box material in a boiling-water reactor environment is that the box plate is difficult to bend to the proper shape after the heat treatment. Because of the structure which is formed after the heating to beta phase with a subsequent rapid cooling to alpha phase, cracks easily occur in the material when this is to be bent into U-shape before the manufacture of a fuel box. Nor does a preliminary heat treatment of the material to increase the ductility give sufficiently good results for the material to be capable of being bent without the risk of cracking. In addition, the possibility of preheating the material is limited by the fact that this heat treatment may deteriorate the corrosion properties of the material.

SUMMARY OF THE INVENTION

The present invention comprises a fuel box and a method for manufacturing zirconium alloy plates for such fuel boxes. The method includes a heat treatment of the plates wherein these are beta-quenched, that is, are heated to the beta-phase region and thereafter rapidly cooled to the alpha-phase region to improve the corrosion properties of the material in a boiling-water reactor environment, and which means that the ductility of the material is not deteriorated by the heat treatment.

The method according to the invention is based on the realization that a special form of Widmanstätten structure, the so-called "basketweave" structure and in particular a finely lamellar basketweave structure is favourable to be able to carry out bending of box plate without the risk of cracking arising. Achieving a finely lamellar basketweave structure with good corrosion and bending properties requires control of the composition of the zirconium alloy and that the heat treatment is carried out with a controlled heat-treatment

temperature and cooling rate. The invention will be described in greater detail below.

During heat treatment of zirconium alloys in the beta-phase temperature range (980°C to 1120°C) followed by rapid cooling to alpha phase, in principle two types of Widmanstätten structures may arise, so-called basketweave structure and parallel-plate structure. The basketweave structure is characterized by a plurality of nucleus formation points and in that the lamellae have grown in several different directions such that the structure resembles a "basket pattern". The parallel-plate structure exhibits grains with lamellae which have grown in parallel through a large part of the beta grain out from the grain boundaries.

The formation of the basketweave structure is associated with a high content of carbon, silicon or phosphorus in the material. These substances are not completely soluble in the beta phase as most alloying elements but may form nucleus formation points for the phase transformation during the temperature reduction. It has been noted that when silicon is the main impurity, rapid cooling from 1050°C leads to a parallel-plate structure, whereas cooling from a higher temperature leads to a basketweave structure (ASTM STP 939 Influence of Impurities and Temperature on the Microstructure of Zircaloy-2 and Zircaloy-4 after the Beta to Alpha Phase Transformation, Charquet et al.). Basketweave structure also occurs in materials with impurity residues from the zirconium manufacture in the form of stringers of volatile substances such as chlorine, magnesium, calcium and potassium, which have been included in the material during the solidification. Normally, remelting of zirconium is carried out to avoid having volatile impurities remaining in the material.

To achieve a beta-quenched material which is ductile and has a basketweave structure, it is suitable to ensure that the zirconium contains small amounts of volatile impurities such

as primarily chlorine, but also magnesium, calcium, sodium and potassium may occur. The contents of these substances should be low, the amount of chlorine should be within the interval 0.5 to 10 ppm and the amount of other volatile impurities should be within the interval 5 to 20 ppm. The melting conditions must be adjusted in order not to obtain too low a content of these substances. Also, the percentage of recirculated material should be kept below 50% since this material contains lower contents of volatile impurities than "newly manufactured" material.

Other elements favourable for the formation of the basketweave structure are carbon, silicon, and phosphorus. The carbon content should be at least 100 ppm and be lower than 200 ppm, the silicon content at least 50 ppm and lower than 120 ppm, and the phosphorus content at least 1 ppm and lower than 30 ppm.

The formation of a favourable structure after beta quenching is further improved by a controlled manufacture of the material. The manufacturing is important since it influences distribution and size of the precipitates and inclusions which have low solubility in the beta-phase region and which thus act as nucleus-formation points during the phase transformation. Of special importance are the heat-treatment and hot-working operations which the material undergoes during the manufacture into plate.

Also heat treatments of the plate which are carried out to manufacture boxes of the plates may influence the properties of the material.

Another factor of importance is the oxygen content of the zirconium alloy. It has been discovered that during beta quenching an enrichment of the oxygen content in the lamellae will occur. If the oxygen content is kept low, at around 600 to 1300 ppm and preferably 900 to 1100 ppm, the ductility of

the material is improved without adverse effect on the strength of the material.

During the manufacture of plate, the hot working of the ingot is important. During this working, a degradation of the solidification structure occurs. The hot working normally occurs in two steps. The first working may occur at 1100° to 1200°C in order for the impurities of silicon to dissolve and be evenly distributed in the matrix and to equalize macro-segregations in the structure.

A second working step is made in the alpha-phase temperature range at 650 to 800°C.

In an intermediate step after the working in the beta-phase temperature range, it is favourable to heat-treat the material at a low temperature in the alpha-phase region to obtain nucleus formation of silicides. This heat treatment may be made within the interval 450 to 550°C for two to five hours.

Other hot working operations which the material undergoes during the manufacturing, such as hot rolling and/or extrusion, should be carried out at such time/temperature conditions in order for the silicides not to grow and coalesce.

During the final beta quenching of the plate in the finished dimension or almost finished dimension, a fast grain growth takes place during the processing in the beta-phase region. Intermetallic precipitates between zirconium and the alloying elements are dissolved in the beta phase, and there is therefore a considerable risk that very large grains which have an unfavourable influence on the structure after cooling are formed. To reduce the grain growth, according to the invention the material shall be maintained for a very short time, about five to fifteen seconds, in the beta-phase region. The composition of the material, and particularly the quantity

of silicon, carbon and phosphorus, together with the quantity of volatile impurities such as chlorine and also magnesium, calcium, sodium and potassium, are important for controlling the structure. The cooling rate from the beta-phase temperature has a great influence on the corrosion resistance of the material, and it has proved that the cooling rate should be moderate to obtain good corrosion resistance. A cooling rate within the interval 5 to 50°C per second gives a good structure and good corrosion properties. The cooling rate should be below 100°C per second since a very rapid cooling has proved to greatly deteriorate the corrosion resistance of the material.

In order to improve corrosion properties and to restore the flatness of the product after beta quenching the material is heat-treated after the beta quenching at a temperature above 600° C in a static furnace or 700° C in a continuous furnace, and in both cases not above 800° C. It is advantageous to cool the material fairly rapidly after this final heat treatment. A cooling rate exceeding 5° per second is preferred.

During the manufacture of boxes, the plates should not be subjected to heat treatments in the temperature range above 770°C.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As starting material, standard sponge zirconium with about 40% recycling material is used, which is at least double melted in conventional manner. During the ingot manufacture, the alloying elements are added to form Zircaloy-2 or Zircaloy-4. The manufactured ingot is forged in the beta-phase region, at a temperature of around 1150°C, to dissolve and distribute phases containing silicon.

Thereafter, a heat treatment at 450 to 500°C may be made for the purpose of precipitating small silicides and secondary-phase particles comprising the alloying elements. This heat treatment may also be omitted.

5

Conventional forging to reduce the dimensions of the material is made in the alpha-phase region to prevent the silicides from growing.

- 10 The forging is reduced additionally by hot rolling for example after preheating at 950° C for 15 minutes or 750° C for 45 minutes to a thickness of about 30 to 20 mm followed by a second hot-rolling operation to a plate thickness of about 6 mm at a maximum temperature of 650°C.

15

A 1020° C solution treatment for 5 to 10 minutes followed by rapid cooling may be added at 30/20 mm thickness in order to homogenize the alloying elements, such as tin, iron, chromium or nickel.

20

The temperature during the hot-rolling steps is kept relatively low to avoid the growth of silicides and other impurities.

- 25 Thereafter, the substance is cold-rolled in a number of steps down to the finished dimension. Between each cold-rolling step, a heat treatment is carried out at about 630°C in a static furnace or 730° C in a continuous furnace.

- 30 During the finishing beta quenching, a structure which improves the corrosion properties and the ductility is to be achieved. The material is heat-treated by allowing a band of the material to pass through a heat source, for example an infrared lamp, and thus be heated to about 1050°C for about 10
35 seconds. Thereafter, the material is cooled when the band leaves the heating zone. The cooling occurs at a rate of about 25°C per second.

The plate material exhibits a microstructure which is characterized by a finely lamellar basketweave structure.

5 The material is heat-treated after the beta quenching at a temperature above 600° C in a static furnace or 700° C in a continuous furnace, and in both cases not above 800° C.

10 To manufacture boxes, the plates shall first be bent into U-shape. The bending may be made without preheating of the plate. Crossplates for boxes with an internal water cross may be preheated at about 200°C before being bent and embossed.

15 To prevent the risk of cracking during the bending operation, the plates must have a good ductility. The occurrence of even very small cracks in the material leads to the material having to be rejected. Microcracks may constitute a problem since they may be difficult to detect. The ductility of the material must thus be sufficiently good to prevent the occurrence of cracking.

20

The bent box halves are joined together by means of TIG welding along the respective sides. The box is shaped to obtain the desired straightness and square dimension. The shaping is performed in a conventional manner by fitting the box onto a mandrel of stainless steel, which is true to gauge, and thereafter heating the package to about 600°C. Since the steel expands more than the zirconium alloy, the dimensions of the mandrel are imparted to the box.

30

CLAIMS

1. A method for manufacturing plate material of zirconium alloy for manufacturing fuel boxes for boiling water reactors, wherein said method comprises working of the material by means of forging, hot rolling and/or extrusion, cold-rolling operations and intermediate heat treatments, as well as a beta quenching of the plate in finished or near finished dimension, **characterized** in that the material comprises, in addition to alloying elements and incidental impurities, also volatile impurities, said impurities comprising 1 to 10 ppm chlorine and 5 to 20 ppm of one or more elements from the group consisting of magnesium, calcium, sodium or potassium, and that the material also comprises 100 to 270 ppm carbon, 50 to 120 ppm silicon, and 1 to 30 ppm phosphorus, and that the beta quenching is carried out in such a way that the material is given a basketweave structure and the material is heat-treated after the beta quenching at a temperature above 600° C in a static furnace or 700° C in a continuous furnace, and in both cases not above 800° C.
2. A method according to claim 1, **characterized** in that the cooling rate of the material after the final heat treatment shall exceed 5°C per second.
3. A method according to claim 1 or 2, **characterized** in that the material comprises 600 to 1300 ppm oxygen.
4. A method according to claim 1 or 2 **characterized** in that the material comprises 900 to 1100 ppm oxygen.
5. A method according to claim 1,2,3 or 4, **characterized** in that beta quenching at final thickness of the material is performed by heating to 900 to 1100°C for at most 15 seconds followed by cooling at a cooling rate below 100°C per second, preferably within the interval 5 to 50°C per second.

6. A method according to any of the preceding claims, **characterized** in that the material is heat-treated between two forging operations at 450 to 500°C to precipitate silicides and secondary-phase particles.

5

7. A fuel box manufactured by material manufactured by means of a method according to one or more of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 97/00667

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C22F 1/18, G21C 3/07

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C22F, G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

METADEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| A | ASTM Special Technical Publication 939, June 1995, Ronald B. Adamson et al, "Zirconium in the Nuclear Industry" -- | 1-7 |
| A | US 4294631 A (ANTHONY ET AL), 13 October 1981 (13.10.81) -- | 1-7 |
| A | EP 0626464 A1 (GENERAL ELECTRIC COMPANY), 30 November 1994 (30.11.94) -- | 1-7 |
| A | EP 0626465 A1 (GENERAL ELECTRIC COMPANY), 30 November 1994 (30.11.94) -- | 1-7 |

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"B" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"T" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search

29 August 1997

Date of mailing of the international search report

30-08-1997

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Nils Engnell
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/00667

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A | GB 1537930 A (AKTIEBOLAGET ASEA-ATOM), 10 January 1979 (10.01.79) -- | 1-7 |
| A | EP 0647724 A1 (COMPAGNIE EUROPEENNE DU ZIRCONIUM CEZUS), 12 April 1995 (12.04.95) -- | 1-7 |
| A | US 4238251 A (WILLIAMS ET AL), 9 December 1980 (09.12.80) -- ----- | 1-7 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

06/08/97

International application No.

PCT/SE 97/00667

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| US 4294631 A | 13/10/81 | BE 880760 A DE 2951102 A GB 2045284 A JP 55100967 A SE 452479 B,C SE 7910623 A | 16/04/80 26/06/80 29/10/80 01/08/80 30/11/87 23/06/80 |
| EP 0626464 A1 | 30/11/94 | US 5361282 A | 01/11/94 |
| EP 0626465 A1 | 30/11/94 | US 5305359 A | 19/04/94 |
| GB 1537930 A | 10/01/79 | BE 839319 A DE 2608824 A FR 2303865 A,B JP 51116106 A NL 7602275 A SE 391952 B,C SE 7502865 A SE 394201 B,C SE 7511523 A | 01/07/76 23/09/76 08/10/76 13/10/76 16/09/76 07/03/77 15/09/76 13/06/77 16/04/77 |
| EP 0647724 A1 | 12/04/95 | FR 2711147 A,B JP 7150315 A US 5478419 A | 21/04/95 13/06/95 26/12/95 |
| US 4238251 A | 09/12/80 | NONE | |

Page Blank (uspto)